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Investigation on Novel Nonlinear Optical L-threonine Calcium Chloride Single Crystal Grown by Solution Growth Technique

R. Vivekanandhan[1, 2], K. Raju[3], S. Sahaya Jude Dhas[4], V. Chithambaram[5*]

[1]Research and Development Centre, Bharathiyar University, Coimbatore, India.
[2]Department of Physics, Sri Krishna Engineering College, Chennai, India.
[3]Departments of Physics, Sri Venkateswara College of Engineering, Chennai, India.
[4] Department of Physics, Saveetha Engineering College – Chennai, India.*
[5] Research and Department of Physics, Dhanalakshmi College of Engineering, Chennai, India.*
**Corresponding author*

Abstract

Nonlinear optical single crystal of L-threonine calcium chloride (LTCC) was grown by slow evaporation technique at ambient temperature. From single crystal X – ray diffraction analysis, the unit cell parameters were calculated. Fourier transform infrared spectroscopic studies were carried out to find the various functional groups present in the grown crystal. The study of optical transmittance of the grown crystal was performed by UV – Vis spectral analysis. The lower cut off wavelength of the grown crystal is found to be at 220 nm. Mechanical strength was assessed by Vickers micro hardness measurements. Thermal analysis was also undertaken for the grown crystal. The biological activities of the sample were also studied. The existence of second harmonic generation signals was observed using Nd:YAG laser with fundamental wavelength of 1064nm possessing SHG efficiency of 1.4 times greater than that of KDP.

Keywords: (A) Crystal Growth, (B) Optical studies, (C) Hardness, (D) Biological activities

INTRODUCTION

In recent times, Nonlinear optical (NLO) materials with desired properties for second harmonic generation (SHG) emerging out of the blend of both organic and inorganic materials have forecasted themselves in the limelight consistently as these materials have received tremendous attention for device fabrications in the field of photonics such as optical computing, optical communications, optical disk data storage, optical logic circuits, optical information processing , optical information processing, high - speed information processing, telecommunication, laser sensing and colour displays [1 - 7]. It has been observed that there is a lot of research progress happening in various labs so as to modify and fine-tune electrical, mechanical and optical properties of prominent NLO materials thereby merging two or more organic and inorganic materials resulting which have the ability to meet the demand of superior quality crystals for the ever growing photonic industries. Of late, novel complexes have been tailored and subsequently synthesized by combining organic and inorganic compounds with various proportions and permutations [8, 9]. As semiorganic crystals posses few added properties which are equally distributed between inorganic and organic materials so that they identify their position of strength to find the way to non linear optical applications. Semi-organic single crystals can also be grown from aqueous solution and the enhanced hardness and the thermal stability make them convenient enough so as to be cut and polished quite easily. In this article, we report a novel semi-organic NLO single crystal of L-threonine calcium chloride grown by slow evaporation method. Moreover, investigations of various characterizations have been carried out so as to confirm the suitability of the crystal to be used for photonic applications.

EXPERIMENTAL SECTION

Crystal growth

L-threonine calcium chloride (LTCC) single crystal was grown from aqueous solution by slow evaporation method. Saturated solution was prepared at ambient temperature by repeated recrystallisation process as it is one of the best methods to improve the purity as well as to remove any insoluble impurities present in the solution. After that, the prepared saturated solution was filtered into a beaker and it was covered with perforated plastic sheet and then housed in a dust free atmosphere so as to ensure solvent evaporation. After a period of 35days, single crystal of $11\times3\times3$ mm^3 size was harvested and the grown crystal is shown in Fig. 1.

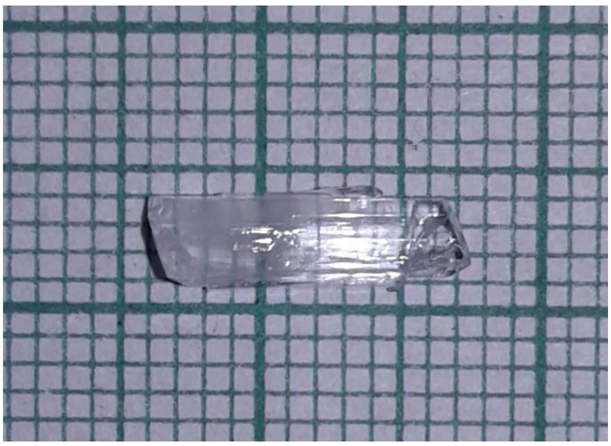

Figure 1. Photograph of as grown single crystal of LTCC

RESULTS AND DISCUSSION

Powder X – ray diffraction analysis

The cell parameter of the grown crystal has been corroborated and it is known from the observed data that the LTCC crystal crystallizes in Orthorhombic system with non-Centro symmetric space group P_1. The cell parameters are identified to be a = 5.18Å, b = 7.79Å, c = 13.71Å, α = 90°, β = 90° γ = 90° and V = 553Å^3. The XRD data obtained for the grown crystal is shown in fig. 2.

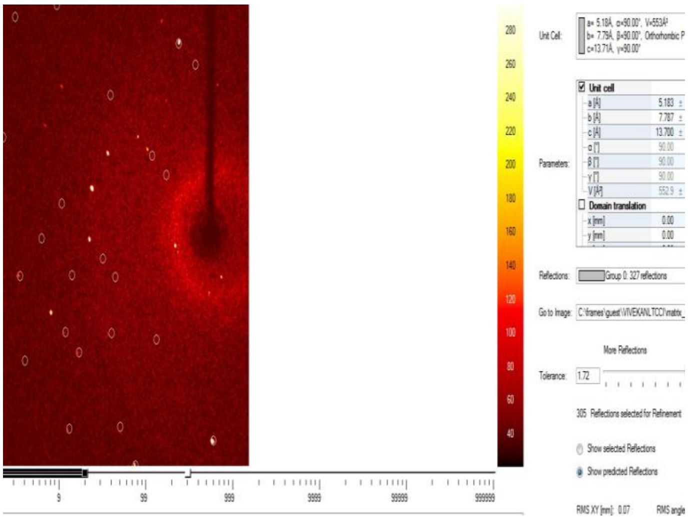

Figure 2. Single crystal XRD pattern

Fourier transform infrared analysis

Fourier transform infrared (FTIR) spectral analysis was carried out using Perkin Elmer FTIR spectrometer by KBr pellet technique in the range of 400 – 4000 cm^{-1}. The recorded FTIR is shown in Fig. 3. The sharp peaks appearing at 3168 and 3028 cm^{-1}are due to the N-H stretching vibration. The peak at 2873 cm^{-1} is assigned to Symmetric stretching of CH_3. The peaks at 2515and 2048 cm^{-1} are assigned to degenerative deformation of NH_3^+ and torsional vibration of NH_3^+. The peak observed at 1480 cm^{-1} corresponds to bending vibration of NH_3^+. The peak at 1455 cm^{-1} is degenerative deformation of CH_3 .The sharp peak appeared at 1042 cm^{-1} is assigned to CH_3 rocking vibration and 933 cm^{-1}is due to the C–C stretching vibration. The peak at 912 is attributed to C-C-H stretching and the medium peak at 870 cm^{-1}corresponds to C–C–N vibration. Out-of-plane bending vibration of CO_2^-vibration peak is located at 767 cm^{-1}. In-plane deformation of COO^- is assigned at 701 cm^{-1} in the spectrum. The peak found at 489 cm^{-1} may be assigned to CO_2^-rocking and the medium band at 870 cm^{-1}corresponds to C–C–N vibration. Out-of-plane bending vibration of CO_2^- vibration peak is located at 767 cm^{-1}. In-plane deformation of COO^- is assigned at 701 cm^{-1} in the spectrum. The peak found at 489 cm^{-1} may be assigned to CO_2^-rocking [11-13].

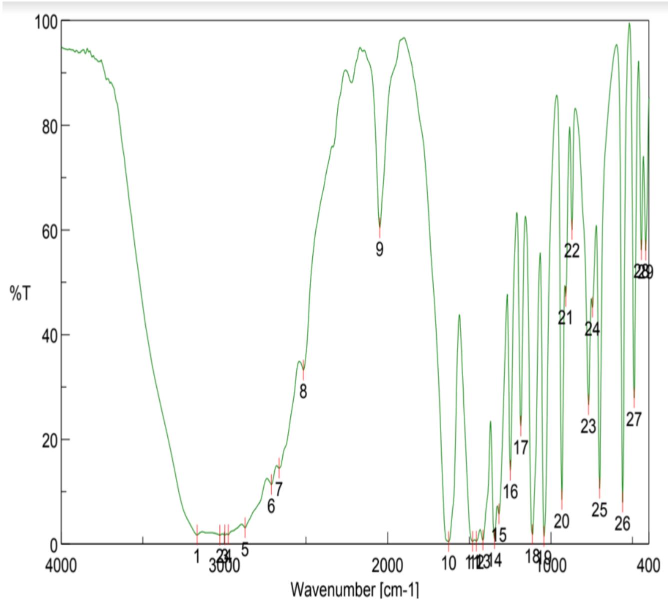

Figure 3. FT – IR spectrum of LTCC crystal.

Optical Transmission studies

NLO single crystals come across to witness their predominant use in optical applications in which the efficiency of optical transmission and the transparency institute a prominent place. The optical transparency of the grown LTCC crystal was analyzed using Varian carry 5E spectrometer in the range of 100-1100 nm. It is found from the data that the crystal is transparent in the wavelength region between 220 and 1100 nm so that it could be used for optoelectronic applications [14-15]. Figure 4 shows the transmission spectrum recorded for the single crystal of LTCC. The cut off value is found to be 220 nm as it could be seen from the figure. As the much needed transmission region is observed for the grown LTCC single crystal in the UV, visible and IR regions it qualifies itself with a proper medium for the fine optical transmission of signals which posses the second harmonic frequencies of Nd:YAG laser [16]. The optical recorded absorption spectrum of LTCC crystal is shown in fig.5.

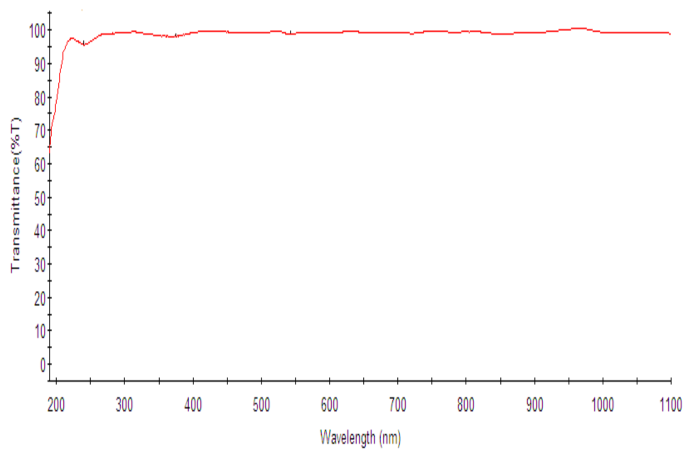

Figure 4. Transmission spectrum of LTCC single crystal

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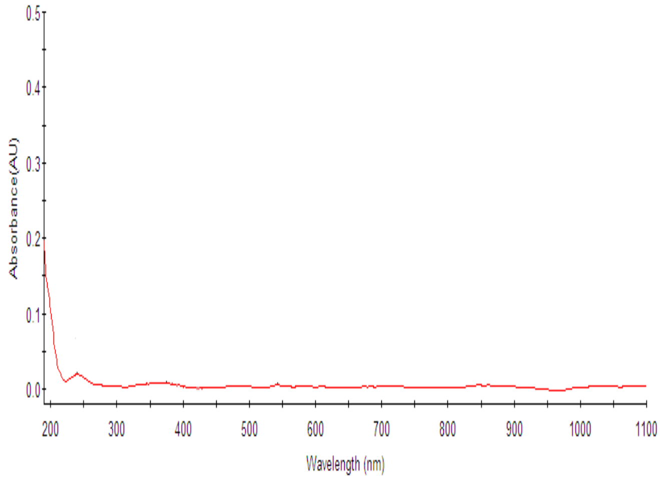

Figure 5. Absorption spectrum of LTCC crystal

Micro Hardness Analysis

One of the methods to determine the mechanical behavior of the grown crystal is micro hardness test. It is correlated with other mechanical properties like elastic constants, yield strength, brittleness index and temperature of cracking [17]. The indentation marks were made on the surface of LHCB single crystal at room temperature by applying load of 25, 50 and 100 g. The Hv is found to increase with increase in the load from 25 to 100 g and crack occurs at higher loads. Mechanical properties of the grown crystal were studied using MH–5 hardness tester. The diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope.

The Vickers micro hardness values were calculated from the standard formula [18]

$$Hv = 1.8544\ (P/d^2)\ kg/mm^2 \quad \text{------} > \text{Eqn. (1)}$$

Where P is the applied load and d is the mean diagonal length of the indentation. The corresponding trace is shown in the Fig.6, from which it is observed that the hardness increases with the increase of load up to 100g and crack occurs at that load. The micro hardness value was taken as the average of the several impressions made.

According to the normal Indentation size effect (ISE), micro hardness of crystal decreases with increasing load and in Reverse indentation size effect (RISE) hardness increases with applied load. In our case, Hv increases with applied load [19].

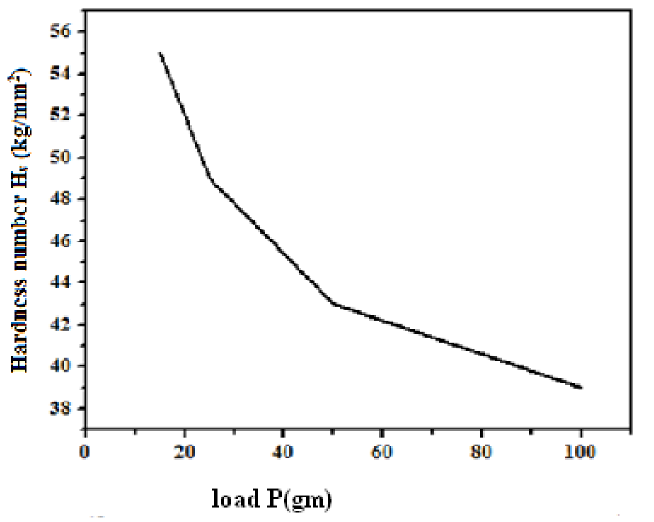

Figure 6. shows the relation between Vickers hardness number vs load of LTCC.

Thermal analysis

Differential Scanning Calorimetric (DSC) study for LTCC was undertaken by a thermal analyzer between the range room temperature and 500 °C. It is observed from DSC curve that there is an endothermic transition peak at 261.9°C which is due to the melting of the material. The degree of sharpness seen in the peak exhibits that the crystal has a very good grade of crystalline nature. It is also known quite clear from the graph that there is no phase transition or decomposition up to the melting point (261.9°C). There is no mass reduction observed up to 275°C which qualifies this material with the possibility of crystallization by melt technique also. Furthermore, it is also known that the crystal is stable in normal humidity conditions withstanding the oxygen atmosphere. Therefore, it is worthwhile to identify from the observed data that the grown crystal has in it the much needed property which can be harnessed for NLO applications. DSC curve of LTCC is shown in Fig.7.

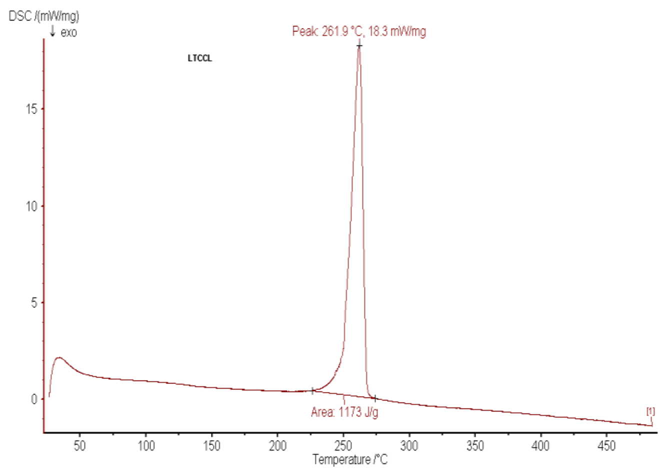

Figure 7. DSC of LTCC single crystal

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Anti–bacterial activity

The anti-bacterial activity of the compound was tested against one gram negative bacterial species and one gram positive bacterial species namely *Escherichia coli* and *Bacillus subtilis* with varying concentration of the compound (LTCC single crystal) that are shown in figure 8(a) and 8(b). The results were shown for the minimum concentration which has the maximum effect. In case of the given compound, maximum antibacterial activity was seen in the concentration of 1mg/ml. The antibacterial activity of the given compound was tested by agar well diffusion method and the results were interpreted by measuring the zone of inhibition (ZOI) formed in agar plate against the particular bacterial specie due to the anti-bacterial effect of the compound.

LTCC has shown the following anti-bacterial activity.

Table 1. (ZOI formed for LTCC in mm)

Compound Name	*Escherichia coli*	*Bacillus subtilize*
LTCC	14	15

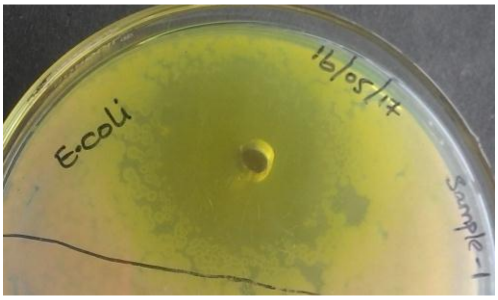

Figure 8 (a) Zone of Inhibition of LTCC in E.coli

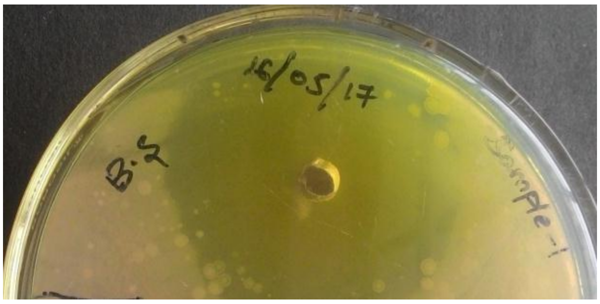

Figure 8(b) Zone of inhibition of LTCC in Bacillus subtiliz

Anti-fungal activity

The anti-fungal activity of the compound was tested against three different fungal species namely *Aspergillus flavus, Trichoderma polysporum,* and *Penicillium cyanum* with varying concentration of the compound and the effect as obtained for the respective sample of LTCC is shown in fig 9(a), 9(b) and 9(c). The results were shown for the minimum concentration which has the maximum effect. In case of the given compound, maximum antifungal activity was seen in the concentration of 1mg/ml.

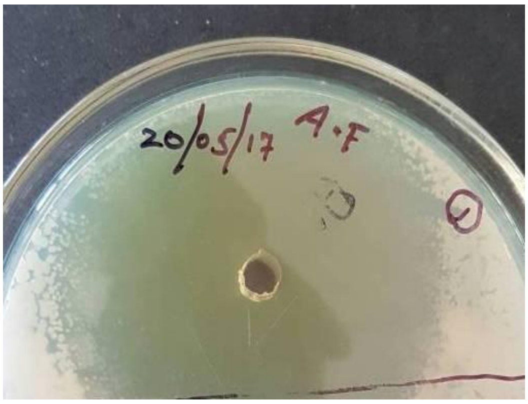

Figure 9(a) Zone of Inhibition of LTCC Aspergillus flavus

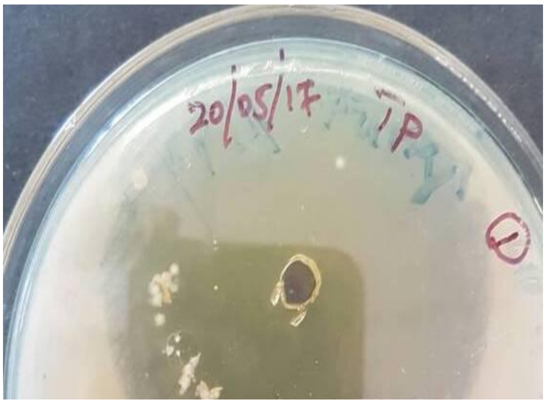

Figure9(b) Zone of Inhibition of LTCC Trichoderma polysporum

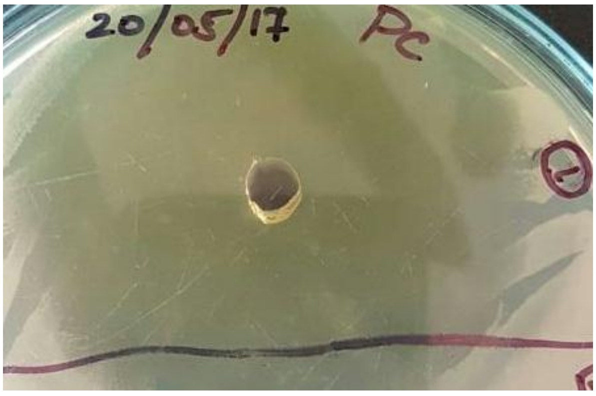

Figure 9 (c) Zone of Inhibition of LTCC Penicillium cyanum

The antifungal activity of the given compound was tested by agar well diffusion method and the results were interpreted by measuring the zone of inhibition (ZOI) formed in agar plate against the particular fungal specie due to the anti-fungal effect of the compound.

LTCC has shown the following anti-fungal activity.

Table 2. (ZOI formed for LTCC in mm)

Compound Name	*Aspergillus flavus,*	*Trichoderma polysporum*	*Penicillium cyanum*
LTCC	20	17	18

FESEM Analysis

The grown crystal was put under Field Emission Scanning Electron Microscopy (FE-SEM) which was to investigate the nature and surface morphology of L-threonine calcium chloride. In order to examine the surface morphology, the transparent region of a good quality crystal was cut into the size of few mm. The FE-SEM micrograph of LTCC crystal is shown in Fig 10. The micrograph gives not only information about the surface morphology but also the presence of imperfections in the crystal. It is observed from the image that there are grain boundaries and distributions over the surface and also a few micro crystals found on the surface of the grown LTCC crystal.

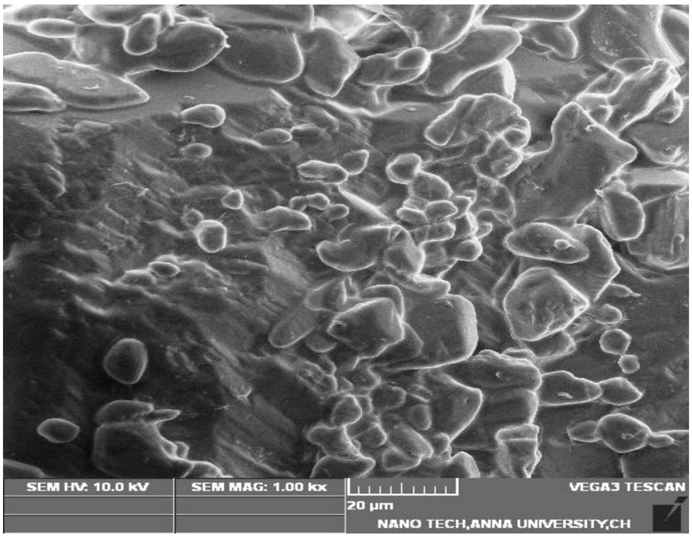

Figure 10. FE-SEM of LTCC crystal

NLO Studies

The study of second harmonic generation was carried out for the grown crystal making use of Kurtz–Perry powder technique. The crystal was powdered into particles of homogenous nature and densely packed between two transparent glass slides. The powder sample with average particle size 100–115μ was illuminated using Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064nm with the pulse width of 8 ns. SHG value of the grown crystal is observed as 36.96 mV that is compared with pure KDP's value of 26.4 mV asserting that the grown crystal has the efficiency of 1.4 times than that of KDP assuring itself to be a potential candidate for photonic applications.

CONCLUSION

The organometallic single crystal of LTCC was grown by slow evaporation solution growth technique. LTCC crystals have orthorhombic system possessed with noncentrosymmetric space group P. Crystallographic data were identified by powder X – ray diffraction studies. The FT – IR spectral studies confirm the presences of functional groups of LTCC crystal. Optical studies confirm that LTCC crystal can be used for optical window applications in the wavelength region 100 – 1100 nm. The microhardness value increases with increase in the load and the Meyer's index number determined for the crystal confirms that it belongs to soft materials category. DSC studies have thrown light on its suitability to with stand the high temperatures encountered in laser experiments. As evidenced by the observed data, and especially due the fact that LTCC crystal has the efficiency of 1.4 times than that of KDP, it is obvious that the grown crystal can be used for optoelectronic devices.

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